Effect of Gamma Irradiation upon Wool Fibers (Special Issue on Physical, Chemical and Biological Effects of Gamma Radiation, IV)

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Wool fibers were irradiated by Co-60 gamma rays, and several radiation effects were measured. The statistical analysis resulted in the conclusion that any appreciable changes in tensile strength and elastic modulus would not be brought about by the irradiation with doses under 10^7 roentgens. The radiation damage of fibers is statistically probable only for 10^8 roentgens or greater doses. The problem of generating crosslinking in wool fibers by irradiation has thus far been neglected in the literature, but the remarkable change in dye-accessibility and solubility of wool fibers caused by the irradiation with smaller doses ranging from 10^3 to 10^5 roentgens suggests the production of crosslinking.

INTRODUCTION

Several publications have been issued in recent years on the effects of high energy radiations, such as reactor radiation, beta and gamma radiation, and high energy x-rays, upon wool fibers[1~9]. The results of these experiments, although made with different species of wool and different radiation sources, agree in the point that the doses up to and equivalent to 10^6 or 10^7 roentgens do not give rise to any appreciable changes in mechanical properties of wool fibers[1,3]. The damage of fibers becomes evident at the dosages over $5 \cdot 10^7$ roentgens, and it is reported that fibrous characteristics are totally destroyed at about 10^9 roentgens.

One of the purposes of the present work is to confirm or to supplement, if any, the knowledge on radiation effects on wool by supplementing the measurements of various properties of wool fibers irradiated mainly with small doses, which, according to the literature, are reported to be incapable of producing any appreciable damage of wool fibers. The changes which come into observation eventually after a series of events initiated by irradiation appear to fall into two distinct classes, that is — crosslinking and degradation. The question as to which of both the effects is predominant, or in what proportion they take place, depends mainly upon the nature of polymers, and there is no useful rule which is universally applicable. So far as wool is concerned, the attention has been concentrated mainly upon the degradation at high doses, and the problem of crosslinking has been left untouched. A series of experiments made in this work also confirm the findings as reported in the literature, but it is interesting to note that some radiation behavior of wool observed here seems to be associable with the production of crosslinking.

1. TENSILE STRENGTH

The change in tensile strength is one of the important effects which indicate

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the radiation damage of fibrous materials. In this case, it is usual to compare the mean value of the strengths of irradiated fibers with that of the original fibers of the same lot. Since it frequently happens in the cases of natural fibers that the strength differs from fiber to fiber to a great extent and the fibers of a specimen cover a wide range of strengths, a great number of measurements is necessary to obtain a reliable average strength. In the present study it was attempted to develop a new method by which the radiation effect can be observed for each individual fiber.

The sample fibers of Australian merino 64's were immersed in an alcohol-benzene mixture for one month, extracted in a Soxhlet's apparatus by the solvent mixture for 60 hours, immersed again in n-hexane for one week, washed with water and dried in an air current at 40°C.

The fibers having a similar fineness were sorted out of the specimen by using a microscope, and were mounted on a frame made from a sheet of thick paper so that the frame covered the middle part of the fibers, whose tips pointed to the same direction, say upwards, as can be seen in Fig. 1. The residual part near to the tip and that near to the root were cut off. The frame was separated into two parts by cutting it along the center line shown in Fig. 1. Each fiber was numbered for differentiation, and the part nearer to the tip was suffixed by U and that nearer to the root by L.

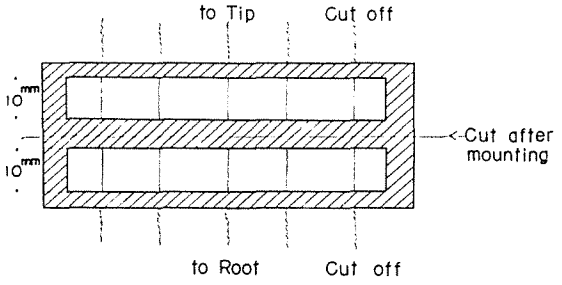

Fig. 1. Mounting of specimen for irradiation and measurement of mechanical properties of wool fibers.

While the U-part was irradiated, the L-part was left in the dark, and vice versa. The radiation dose was changed in 6 steps from 10^3 to 10^8 roentgens. After being irradiated the load-elongation curve of the irradiated part, say U, and that of the unirradiated part, say L, of the same fiber were measured, and the ratio of the irradiated strength to the original strength was determined. About thirty fibers were subjected to the measurements to obtain an average ratio. In another set of fibers the L-part was irradiated and the U-part left in the dark, and the ratio of strengths was determined as before. The wet strength ratios were also measured in the same way.

Measurements of load-elongation curves were made with an Instron type tensile tester in a room conditioned at 20°C and 65% R. H. The span length was 10 mm. and the rate of expansion 20 mm/min.

The gamma ray facility with about 2 kilo-Curies of Co-60 was employed for

irradiation. Thirty-seven pencils of Co-60, each of which, having a nominal rating of 61.7 Curies (June, 1957), is 1.2 cm in diameter and 26 cm in length, were mounted in a circular holder. The sample was irradiated in the center of a container which was placed in the middle of the irradiation chamber. The distribution of gamma ray dose in the chamber is satisfactorily uniform, and the dose rate is about $1.4 \cdot 10^5$ roentgens per hour at the center of the chamber throughout the present work*.

The strength ratios at various doses are shown in Table 1 and Figs. 2 and 3. The results are not simple, but the ratio rises and falls within the region of doses from 0 to 10^6 roentgens. Statistical analyses are necessary for the interpretation of the results.

The level of significance for rejection of a null-hypothesis stating that the difference in average ratios is not significant is too high in the cases of radiation doses up to 10^6 or 10^7 roentgens, as can be seen in Table 1. Only in the case of 10^8 roentgens the change in the strength brought about by the irradiation is supported by a statistically sufficient confidence.

Our experiments which have been done in a different way on the tensile strength came eventually to the same results as those of other authors. However, it is interesting to think over the effects, which might be brought about by the doses up to 10^6 or 10^7 roentgens, because it is not natural to assume that there is

Table 1. Effect of Co-60 gamma radiation upon tensile strength of wool.

Dose (r)	Dry			Wet		
	Ratio of strength[1)]	Confidence limit	Level of significance	Ratio of strength	Confidence limit	Level of significance
Upper part was irradiated						
0	1.088	±0.1136	—	1.040	±0.1191	—
10^3	0.995	±0.0512	0.20	0.920	±0.0818	0.10
10^4	1.016	±0.0676	0.30	1.029	±0.2122	>0.50
10^5	1.178	±0.0988	0.30	1.097	±0.1097	>0.50
10^6	1.035	±0.0998	0.50	0.870	±0.1379	0.10
10^7	0.944	±0.1509	0.20	0.853	±0.1508	0.05
10^8	0.706	±0.0609	0.001	0.310	±0.0220	0.001
Lower part was irradiated						
0	0.951	±0.0884	—	1.019	±0.1168	—
10^3	0.931	±0.1287	>0.50	1.015	±0.0811	>0.50
10^4	1.055	±0.0874	0.10	1.112	±0.1038	0.30
10^5	1.008	±0.1072	0.40	1.155	±0.1582	0.20
10^6	0.981	±0.0930	>0.50	1.000	±0.1466	>0.50
10^7	0.914	±0.1448	>0.50	0.761	±0.1296	0.01
10^8	0.797	±0.0749	0.01	0.358	±0.0238	0.001

1) Ratio of the strength of irradiated part to that of unirradiated part.

* The details of the irradiation facility have been reported by Shimizu and his collaborators[12,13].

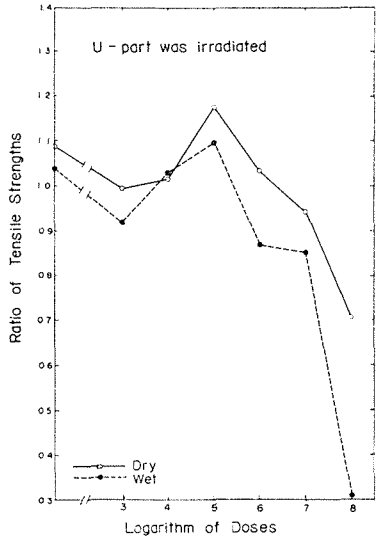

Fig. 2. Ratio of the strength of irradiated part to that of unirradiated part as a function of radiation dose. U-part was irradiated and L-part unirradiated.

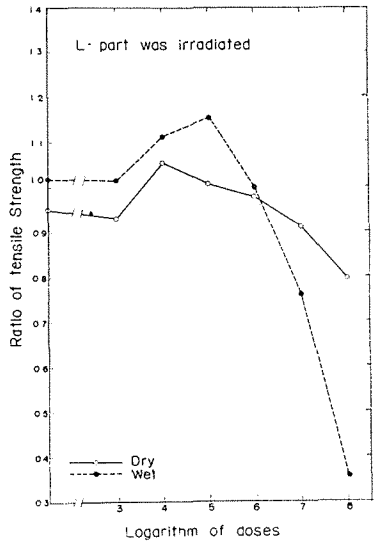

Fig. 3. Ratio of the strength of irradiated part to that of unirradiated part as a function of radiation dose. L-part was irradiated and U-part unirradiated.

no change up to this dose and suddenly the damage occurs when the dose exceeds the threshold.

There will occur the break of fiber at the weakest point existing within the span length. Now, it would be possible to assume that a new weakest point which is weaker than the originally existed one is generated after a period of time of irradiation. This means that the weakening of fiber cannot be observed until a certain period of time passes away. This results in an induction period occasioned thereby. If the crosslinking and degradation can happen simultaneously, as is mostly the case in polymers, the effect of crosslinking, even though it might happen to some extent, would not be evidenced, since the rupture occurs at the weakest point existing in the material. No appreciable change in elongation at break was observed either up to the dose of 10^7 roentgens. This induces us to study further other radiation effects.

2. INITIAL MODULUS

The initial moduli of fibers were determined by means of the load-elongation curves. In Fig. 4 the ratio of modulus of the irradiated part to that of the unirradiated part of the same fiber in dry and wet state is plotted against the radiation dose. Each point in the figure is the mean value of measurements of about thirty fibers. The analysis results in the same conclusion as in the case of breaking strength. The decrease of modulus by irradiation is statistically probable only for 10^8 roentgens or greater doses.

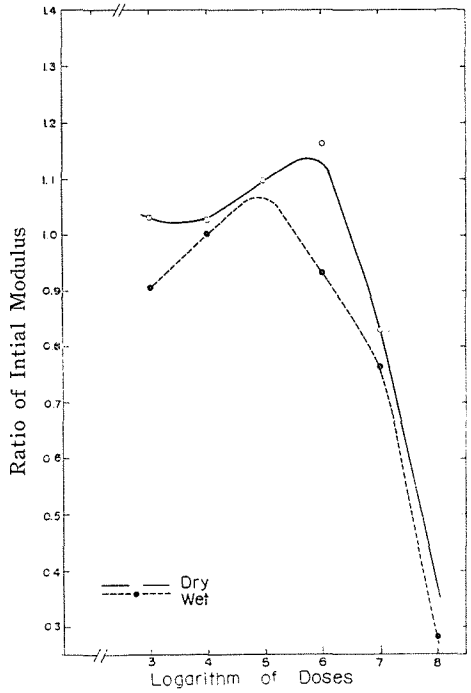

Fig. 4. Ratio of initial modulus of irradiated part to that of unirradiated part as a function of radiation dose. U-part was irradiated and L-part unirradiated.

3. DYE ABSORPTION

Contrary to the mechanical properties, the dyeing property of wool fiber is greatly affected by irradiation even at low doses where any changes in mechanical properties are not noticeable. The rate of dye absorption is strongly depressed by irradiation with Co-60 gamma radiation of low doses from 10^3 to 10^5 roentgens. Two dyestuffs, Ponceau Crystal (C. I. Acid Red 44) and Carbolan Brilliant Green 5G (C. I. Acid Green 28), were used.

Figs. 5 and 6 show the take-up curves of wool irradiated with various doses, and Fig. 7 shows the plotting of time for taking up half the amount of dye against the radiation dose.

The dye absorption is strikingly suppressed at the range of doses from 10^3 to 10^5 roentgens, but fibers regain dye accessibility at higher doses. It is interesting to note that at 10^8 roentgens, where the tensile strength, elongation at break and Young's modulus are remarkably affected, the absorption of dyes becomes even greater than the unirradiated fibers.

It is important to suggest here that two kinds of effects might occur in parallel in wool during the irradiation. The first effect as manifests as an evident decrease in dye accessibility at lower doses may not be altogether independent of crosslinking. On the other hand, the remarkable increase in the take-up at higher doses seems to be associated with strong structural damage of fibers.

It is interesting to note that the increase in accessibility to dyes of the highly

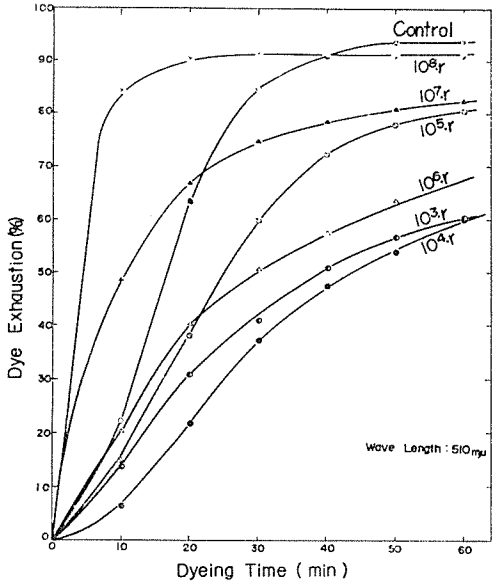

Fig. 5. Plots of dye-exhaustion against time for wool irradiated with various doses. Dyestuff is Ponceau Crystal.

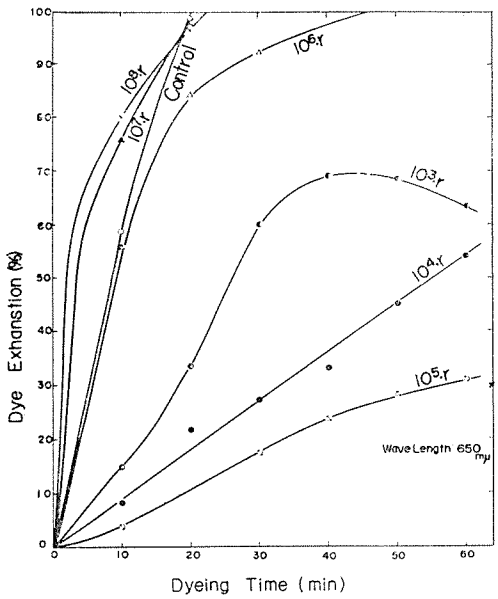

Fig. 6. Plots of dye-exhaustion against time for wool irradiated with various doses. Dyestuff is Carbolan Brilliant Green 5G.

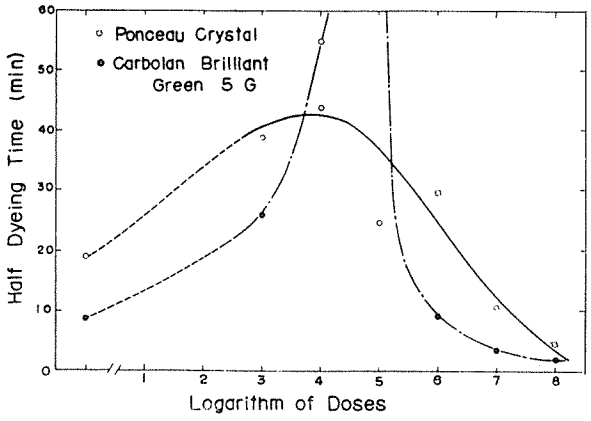

Fig. 7. Plots of time for exhaustion of half the amount of dyes against the radiation dose.

irradiated fibers is so great that the bilateral structure is hardly visualized by the partial staining. Thus the cross-sections of fibers irradiated with a dose of 10^8 roentgens are stained uniformly in dark tone even under the condition which does not give rise to the staining of unirradiated fibers, as can be seen in Fig. 8.

4. SOLUBILITY

Solubility test is one of the useful methods to presume the change in structure of high polymers. The solubility of wool irradiated at various doses in the mixtures, that is — urea-sodium bisulphite and urea-sodium metabisulphite, is shown

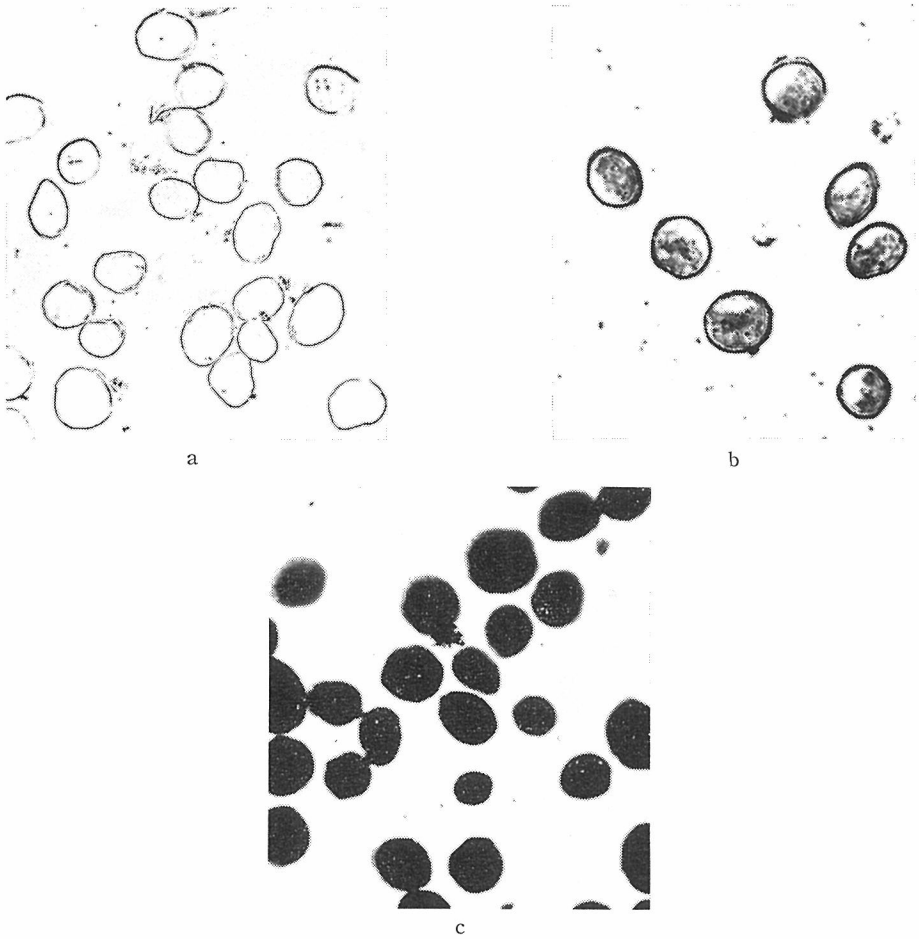

Fig. 8. Staining of cross-sections of irradiated fibers with Methylene Blue under a condition which does not cause the staining of unirradiated fibers.
(a) Unirradiated fibers. (b) Fibers irradiated with 10^7 roentgens. (c) Fibers irradiated with 10^8 roentgens.
(The cross-sections mounted on a slide were stained by 0.01% solution of Methylene Blue at 60–70°C for two hours, and washed with distilled water).

Table 2. Urea-bisulphite and urea-metabisulphite solubility of wool fibers irradiated with various doses.

Dose (r)	0	10^3	10^4	10^5	10^6	10^7	10^8	note
Solubility (%)	4.83	1.80	3.50	4.70	5.55	30.68	100	$NaHSO_3$
	10.40	8.69	4.05	6.11	8.60	30.07	100	$Na_2S_2O_5$

in Table 2. It is important to see that the solubility minimum is found at the doses ranging from 10^3 to 10^5 roentgens. The result seems to be compatible with that of the dye accessibility.

There would be a number of elements which influence the solubility of high polymers, and the crosslinking is only one of them, but, as described before,

the changes induced by irradiation are eventually ascribed to crosslinking and degradation. In this meaning it would be natural to assume that the evident decrease in solubility at the doses from 10^3 to 10^5 roentgens suggests the change in structure such as that resulting from the production of crosslinking. The rapid increase in solubility at higher dosages can be ascribed to the destructive damages caused by the radiation.

EXPERIMENTAL

Dyeing of wool by Ponceau Crystal and Carbolan Brilliant Green 5G. 250 ml of bath liquor containing 0.01 g of dye were used for 1 g of wool. The bath was heated to boiling during dyeing. Distilled water was supplied from time to time to make up the loss by evaporation. No auxiliary was employed. 5 ml of bath liquor were taken every ten minutes for photometry, for which a Beckmann's photoelectric spectrophotometer was used. The optical densities at the wavelength of absorption maximum were used to calculate the take-up percentage. λ_{max} of Ponceau Crystal is 510 mμ, and that of Carbolan Brilliant Green 5G 650mμ.

Staining of cross-sections by Methylene Blue. Cross-sections mounted on a slide were dipped in a dish containing 0.01% solution of Methylene Blue at 60–70°C for two hours. The pH of the liquor was 6.5. The slide was then taken out of the dish and transferred into another dish containing distilled water and left to stand for 5 min. to allow the loosely fixed dyestuff to diffuse out of the cross-sections. This procedure of washing was repeated three times and the cross-sections were dried in air. The dye came out almost completely from the cross-sections of the unirradiated fibers.

Measurement of solubility of wool. The method of Lees and Elsworth[10] was employed. Because it is reported that the solubility of wool is considerably influenced by heating in air[11], each sample was dehydrated by placing it upon phosphoric anhydride in a desiccator at room temperature until the constant weight is reached, and the dry weight was determined. Then the sample was introduced into the urea-sodium bisulphite or urea-sodium metabisulphite solution kept at 65±1°C, which had been prepared by dissolving 50 g of urea and 3 g of sodium bisulphite or sodium metabisulphite in 100 ml of distilled water and adjusted to the pH value of 7.0±0.1 by neutralizing with 5N caustic soda solution. After being immersed in the solution for one hour, the residue was separated from the liquor by filtering it with a glass filter under suction, and washed on the filter three times with 25% urea solution and six times with distilled water for fifteen seconds each time. The wet sample was dried in an air current at 40°C, and dehydrated further up to the constant weight by phosphoric anhydride as before to determine the dry weight.

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